PB82-224361

Sorption of Carbon Tetrachloride, Ethylene Dibromide and Trichloroethylene on Soil and Clay

(U.S.) Environmental Monitoring and Support Lab.
Las Vegas, NV

Jun 82

U.S. Department of Commerce
National Technical Information Service
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1. REPORT NO. EPA-600/J-81-560	2. Journal Article
3. REC	PB82-224361
4. TITLE AND SUBTITLE: Sorption of Carbon Tetrachloride, Ethylene Dibromide, and Trichloroethylene on Soil and Clay	5. REPORT DATE: June 1982
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S): Robert D. Rogers and James C. McFarlane	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS: Environmental Monitoring Systems Laboratory, US Environmental Protection Agency, Las Vegas, Nevada 89114	10. PROGRAM ELEMENT NO.
	11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS: same	13. TYPE OF REPORT AND PERIOD COVERED: inhouse - journal article
	14. SPONSORING AGENCY CODE: EPA/600/02

15. SUPPLEMENTARY NOTES: Published in Environmental Monitoring and Assessment 1 (1981) 155-162

16. ABSTRACT

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17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

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NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA 22161

18. DISTRIBUTION STATEMENT: release to public	19. SECURITY CLASS *(This Report)*: unclassified	21. NO. OF PAGES
	20. SECURITY CLASS *(This page)*: unclassified	22. PRICE

EPA Form 2220-1 (9-73)

EPA-600/J-81-560
Journal Article

SORPTION OF CARBON TETRACHLORIDE, ETHYLENE DIBROMIDE, AND TRICHLOROETHYLENE ON SOIL AND CLAY

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Abstract. The sorption of carbon tetrachloride, ethylene dibromide, and trichloroethylene in two silty clay loam soils and aluminium (Al^{3+}) or calcium (Ca^{2+}) saturated montmorillonite clay was studied. When the adsorbents were exposed to environmental levels of these chemicals (10 to 1000 ppb in water) the amounts of each of the chemicals sorbed were 6% or less of that available except for a 17% sorption of trichloroethylene by Al-saturated clay. In the case of the Ca-saturated clay, there was no apparent sorption of carbon tetrachloride or trichloroethylene. When soil sorption was normalized based on the soil organic carbon content (K_{oc}), a correlation was found between the K_{oc}, water solubility, and octanol/water partitioning coefficients of the chemicals. However, carbon tetrachloride did not behave according to with the predicted relationships.

1. Introduction

As interest in the fate of organic pollutants in the environment increases, special concern is justified for chemicals which are known to be, or are suspected of being, carcinogenic. For our initial studies we selected benzene, carbon tetrachloride, ethylene dibromide, and trichloroethylene. These chemicals were picked because they ranked high on the list of carcinogens in terms of activity and quantities produced and released [1]. Their elevated volatility and low water solubility make them difficult to work with and may have precluded them from other environmental studies. Our interest was not the fate of chemicals resulting from a large spill onto the soil, but rather the behavior of those quantities which could be dissolved in surface water or scrubbed from the atmosphere by precipitation.

In a previous study with benzene, experimental and interpretational procedures were developed which allowed for a more rapid evaluation of the sorption characteristics of chemicals [2]. The object of this report is to present the sorption-partition constants for carbon tetrachloride, ethylene dibromide, and trichloroethylene in soils and clay, as well as the relationships between the soil sorption constants and some physical properties of the chemicals which were investigated. These data add to an understanding of the relationships between physical and chemical properties upon which predictions of the fate of organic chemicals in soil will be based.

2. Materials and Methods

The adsorbents used for the study included two soils (Overton series from southeastern Nevada and Hastings series from Nebraska), and montmorillonite clay (montmorillonite

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Environmental Monitoring and Assessment 1 (1981) 155–162. 0167–6369/81/0012–0155$01.20.

25; Upton, Wyoming; Wards Natural Science Establishment). Before use, the clay was saturated with either Al^{3+} or Ca^{2+}. The methods used to prepare the soils and clay were reported previously [2]. Chemical and physical properties of these adsorbents are found in Table I.

TABLE I

Physical and chemical properties of adsorbents

Adsorbent	% Sand	% Clay	% Organic carbon	Cation exchange capacity, mequiv/100 g	pH
Hastings silty clay loam	1	31[a]	2.6	17	5.6[c]
Overton silty clay loam	15	34[a]	1.8	29	7.8[c]
Al-saturated montmorillonite	0	100	0[b]	80[b]	4.2[d]
Ca-saturated montmorillonite	0	100	0[b]	80[b]	6.6[d]

[a] Montmorillonitic in character.
[b] Assumed value.
[c] 1 : 5 soil-water solution.
[d] 1 : 50 clay-water solution.

Carbon tetrachloride, ethylene dibromide and trichloroethylene were obtained from New England Nuclear premixed in distilled H_2O. Each chemical was uniformly labeled with 0.10 mCi of ^{14}C, mixed with 20 ml distilled H_2O and sealed in glass ampules. Specific activity of the chemicals were: carbon tetrachloride, 4.7 mCi/mmol; ethylene dibromide, 20.0 mCi/mmol; trichloroethylene, 2.1 mCi/mmol. Upon arrival, the solutions were frozen at $-5\,^{\circ}C$ until needed. Three solution concentrations of each chemical were used; 10, 100, and 1000 ppb (W/W) in the case of carbon tetrachloride and ethylene dibromide and 100, 500, and 1000 ppb (W/W) for trichloroethylene.

Sorption of the chemicals to the adsorbents was determined by triplicate batch equilibration. Time periods for equilibration were 16, 42, and 144 h for all the chemicals. The amount of chemical associated with an adsorbent was determined by oxidation followed by liquid-scintillation. The techniques used for this study together with the methods used to generate Freundlich sorption constants (K_f and $1/n$) were carefully detailed in a previous report [2].

3. Results and Discussion

An investigation of K_f values versus adsorbent-chemical equilibration times was made so that time dependent sorption could be determined for each of the chemicals. In general, there were no significant changes (greater than 2X) of K_f values with time. For convenience, 16 h was chosen for the equilibrium time period.

When using radio tracers it is also important to determine K_f values with time since a drastic change in these values could indicate that the subject chemical is being modified. This was found in a previous study with benzene [2]. In this study it is unlikely that any of the slight variations of K_f values with time would be related to a sorption of ^{14}C degradation compounds. Carbon tetrachloride has been reported to have a half-life in H_2O some 7000 to 70 000 years [3, 4] though the rate of hydrolysis can be accelerated by the presence of iron, zinc, and other metals [4]. Biodegradation of carbon tetrachloride appears possible in waste treatment with a suitable population of adapted micro-organisms [5]. The halflife of ethylene dibromide due to hydrolysis is of the order of 5 to 10 days [6]. Other reports have shown that in a soil-water culture a concentration of 5.75×10^{-4} of ethylene dibromide required 2 months for degradation [7]. Evidence suggests that trichloroethylene has a half-life in water that can exceed many months [8]. This chemical also appears to be immune to biodegradation [8].

The Freundlich sorption constants, K_f and $1/n$, were determined by linear regression [2]. In all cases (except Ca-saturated clay with ethylene dibromide) the replicate analyses were within 20%, and the goodness of linear fit as indicated by r squared was greater that 98%. An example of a Freundlich plot of these data is presented in Figure 1. In general, the K_f values are proportional to the relative sorptive capacities

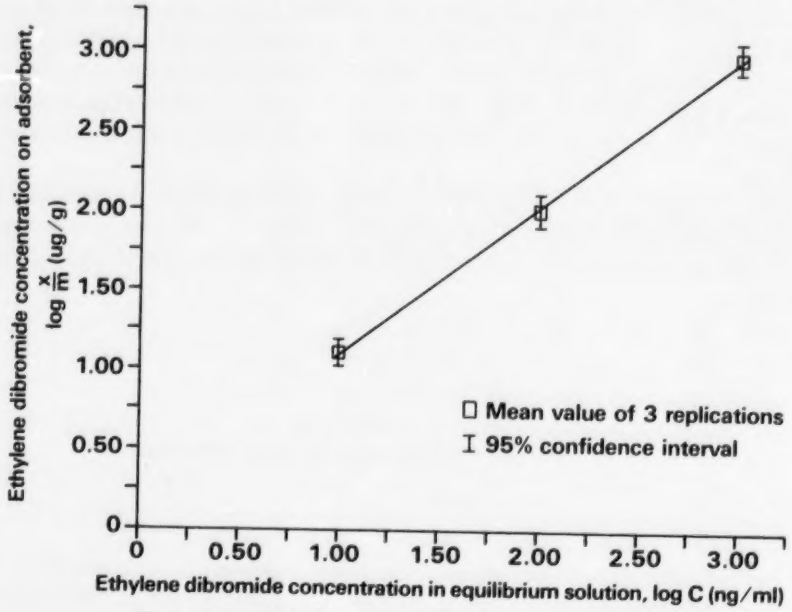

Fig. 1. Freundlich plot for ethylene dibromide on Overton silty clay loam.

of the adsorbents. For these chemicals the K_f values (Table II) indicate that only minimal sorption would occur in soil or clay. Indeed in no case did the sorption of chemicals to adsorbents exceed 6% (Table III) except for a 17% sorption of trichloroethylene by

TABLE II

Freundlich constants for carbon tetrachloride (CT), ethylene dibromide (EDB) and trichloroethylene (TCE) after 16 h of incubation

	CT		EDB		TCE	
Adsorbent	K_f	$1/n$	K_f	$1/n$	K_f	$1/n$
Hastings silty clay loam	0.62	1.08	1.31	0.93	3.89	0.82
Overton silty clay loam	1.18	1.04	1.49	0.92	1.57	0.93
Al-saturated montmorillonite	1.75	0.88	0.47	1.04	6.96	0.92
Ca-saturated montmorillonite	NS[a]		0.05[b]	1.03[b]	NS	

[a] NS means No Apparent Sorption.
[b] Values not considered statistically valid.

Al-saturated clay. The Ca-saturated clay was ineffective as an adsorbent. In another study [2], both Al^{3+} and Ca^{2+} clay treatments sorbed more benzene than the soils, with the Al-saturated clay having the greater sorptive capacity. The mechanism causing the increased sorption by Al-saturated clay is not understood. It is possible that claymetal complexes could be responsible for a significant amount of neutral organic compound sorption.

There is evidence that the sorption of neutral organic chemicals by soils can be correlated with the soil organic carbon content [10, 11]. A normalized sorption constant (K_{oc}) based upon soil organic carbon content can be obtained by use of the following equation:

$$K_{oc} = \frac{K_f \times 100}{\%_{oc}}$$

TABLE III

Percent of available chemical sorbed by adsorbents

	Adsorbent			
Chemical	Hastings silty clay loam	Overton silty clay loam	Al-saturated montmorillonite	Ca-saturated montmorillonite
Carbon tetrachloride	4	6	4	NS[a]
Ethylene dibromide	4	4	2	0.3
Trichloroethylene	6	4	17	NS

[a] NS means No Apparent Sorption.

where K_f = the Freundlich constant,
$\%_{oc}$ = the percent soil organic carbon.

The K_{oc} values have a potential use in predicting the fate of a whole class of organic chemicals in soil [11]. Because of the importance of K_{oc}'s, there has been some effort made to use other measurable physical properties of chemicals to estimate K_{oc} values. For instance, Briggs [12] reported a relationship between soil sorption of organic chemicals and their octanol/water partition coefficients (K_{ow}). Karickhoff and co-workers [11] found that K_{oc} can be estimated from K_{ow} values by use of the following equation:

$$K_{oc} = 0.63\ K_{ow}.$$

Another relationship between K_{oc} and the water solubility of a chemical was presented by Kenaga [13]. He postulated the following equation to describe this relationship:

$$\log K_{oc} = 3.64–0.55\ (\log Ws)$$

where Ws = water solubility of the chemical.
Karickhoff [11] suggested the use of a different equation:

$$\log K_{oc} = 0.54\ (\log S) + 0.44$$

where S = water solubility expressed as mole fraction.

TABLE IV

Physical properties of evaluated chemicals

Chemical	Water solubility: Mole fraction ($\times 10^6$)	Water solubility: ppm	Vapor pressure (mmHg)	Octanol/water partition coefficient
Carbon tetrachloride	93	800[a]	115 @ 25C[c]	537[e]
Ethylene dibromide	320	3370[a]	12 @ 25C[d]	58[f]
Trichloroethylene	149	1100[b]	58 @ 20C[b]	195[f]

[a] From E. E. Kenaga [13].
[b] From R. Johns [6].
[c] From R. Johns [4].
[d] From B. B. Fuller [14].
[e] From C. T. Chiou *et al.* [15].
[f] From A. Leo (personal communiction).

We used all these equations to calculate K_{oc} values for the chemicals used in this study. The physical properties of carbon tetrachloride, ethylene dibromide, and trichloroethylene required to make the computations are presented in Table IV. In addition, the average K_{oc} values were experimentally determined from the soil K_f constants and organic carbon content. Table V shows these values along with data for benzene, obtained from a previous study [4].

A wide range of K_{oc} values were obtained for each chemical depending upon the predictive equation used. In general, the K_{oc} prediction based on K_{ow} gave the best

comparison. This is of interest because it is now possible to mathematically predict K_{oc} constants [16]. The methods using water solubility yield K_{oc} values which bracketed the measured K_{oc} values. These data (Table V) show that carbon tetrachloride did not sorb to the extent predicted. Perhaps additional studies should be conducted to evaluate the reason for this large difference.

TABLE V

K_{oc} values as predicted by chemical solubility in H_2O and octanol/water partition coefficient (K_{ow})

Chemical	K_{oc}[a] Experimentally obtained	K_{oc} predicted by H_2O solubility		K_{oc} Predicted by K_{ow}[c]
		Method 1[c]	Method 2[d]	
Benzene	96[b]	186	71	81
Carbon tetrachloride	45	384	88	338
Ethylene dibromide	66	211	50	36
Trichloroethylene	188	322	74	123

[a] Average value of K_{oc}'s from the two soil adsorbents.
[b] K_{oc} value for benzene was obtained from R. D. Rogers *et al.* (1980).
[c] From S. W. Karickhoff *et al.* [11].
[d] From E. E. Kenaga [13].

Another effort was made to determine the correlation between the air/water partitioning of a chemical and its K_{oc} values. Such an interaction would be useful because the terrestrial exposure to chemicals can be from contaminated water sources, i.e., groundwater or precipitation. The chemical partitioning between the water and air control the availability of a compound for soil sorption.

The air/water partition constant (H) for a chemical can be calculated by the equation [17]:

$$H = \frac{C\,\text{air}}{C\,\text{water}} = \frac{16.04\,PM}{TS}$$

where C air and C water = equilibrium concentrations in the air and water phases,
P = vapor pressure of the pure solute in mm of Hg,
M = gram molecular weight of the solute,
I = temperature in K,
S = solubility of the solute in water (ppm).
Drilling [17] successfully demonstrated that experimentally derived constants compare with those which had been calculated by this equation.

A regression plot of K_{oc} versus H was generated to determine a relationship between these constants (Figure 2). Chemicals used for the calculation included those fom Table V and two chemicals (anthracene and phenanthrene) whose K_{oc} values were reported by Karickhoff [11]. The regression fit was poor ($r^2 = 0.46$) thus indicating a questionable relationship between the two constants for these chemicals.

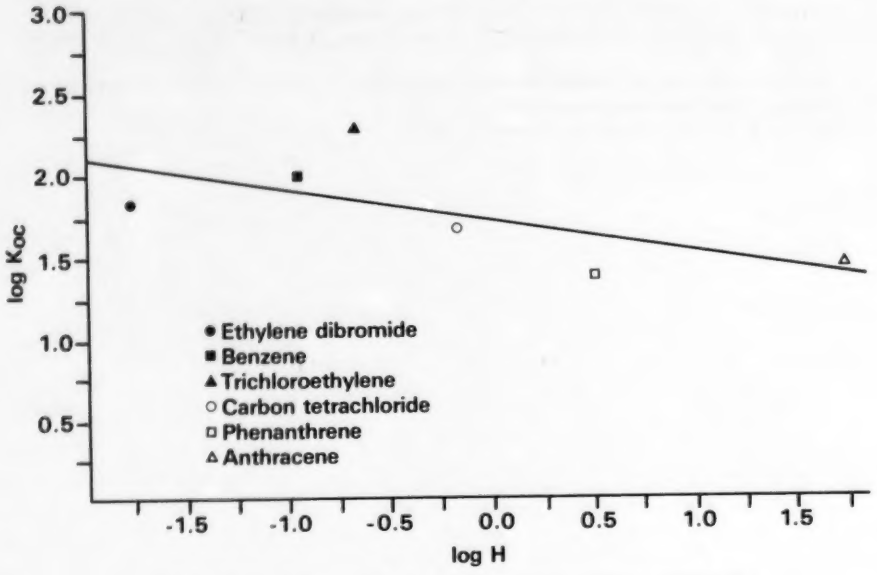

Fig. 2. Sorption K_{oc} as a function of the air/water partition constant (H).

There are undoubtedly other relationships between organic chemicals and various partition constants. As more partition data are collected on a variety of chemicals, these relationships will become obvious. Data from this study support the methods used to estimate soil sorption of neutral organic chemicals. In addition, it should add more interest to sorption potential of metal saturated clay.

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